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EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE.

COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

	PAGE.
Hydrofluoric Acid. By G. de Chalmot	415
Nitrogen Assimilation in the Cotton Plant. By Charles E. Coates and W. R. Dodson	425
Determination of Lactose in Milks by Double Dilution and Polarization. By H. W. Wiley and E. E. Ewell	428
A Study of the Zirconates. By F. P. Venable and Thomas Clarke	434
A Modified Ammonium Molybdate Solution. By A. L. Winton	445
On the Estimation of Sulphur in Pyrites. By Thomas S. Gladding	446
Further Notes upon the Fats contained in the Tuberculosis Bacilli. By E. A. de Schweinitz and Marion Dorsett	449
The Cassel-Hinman Gold and Bromine Process. By Parker C. McIlhiney	451
A Simple Method for Determining the Neutrality of the Ammonium Citrate Solution Used in the Analysis of Fertilizers. By. N. W. Lord	457
The Copper Assay by the Iodide Method. By Albert H. Low	458
On Two Sources of Error in Sugar House Analyses. By Edmund C. Shorey	462
Review: Berthelot's Contributions to the History of Chemistry	466
Books Received	474

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PAPERS ACCEPTED FOR PUBLICATION:

On the Reaction between Carbon Tetrachloride and the Oxides of Niobium and Tantalum. By M. Delafontaine and C. E. Linebarger.

A Simple Form of Gas Regulator. By Ludwig Saarbach.

A Method for Separating the "Insoluble" Phosphoric Acid in Mixed Fertilizers derived from Bone and Other Organic Matter, from that derived from Rock Phosphate. By A. P. Bryant.

Sources of Error in Volhard's and Similar Methods of Determining Manganese in Steel. By George Auchy.

The Effect of Acidity on the Development of the Nitrifying Organisms. By E. E. Ewell and H. W. Wiley.

Issued with May Number, 1

Proceedings.

COUNCIL.

The Council has decided to hold the summer meeting at Buffalo, August 21 and 22.

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MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

A regular meeting was held February 13th, 1896. As the meeting was devoted mainly to social purposes and the inauguration of the newly elected president, Dr. E. A. de Schweinitz, it was held at the rooms of The Washington Down Town Lunch Club. After the transaction of necessary business a lunch was served which was enjoyed by thirty-one members. The following persons were elected to membership: Clinton P. Townsend, S. S. Voorhees, and Dr. F. K. Cameron.

The Presidential address before the Washington Section was delivered by the retiring President, Professor Charles E. Munroe, at a special meeting held Friday, February 21, the subject being "The Development of Smokeless Powders." The lecturer sought to show that the necessity for a high-power, smokeless propellent had been created by the mechanical perfection to which ordnance had attained and the precision of the weapons and the instruments by which they were directed; that the possible production of such propellent was dependent on the discovery of guncotton, nitroglycerol, and certain nitro-substitution compounds, and the improvements in their manufacture; that the possibility of producing uniform and reliable propellents was dependent on the invention of pressure gauges and velocimeters; and that the possibility of their economical production was dependent on the invention of mechanical mixers and formers applied in other arts. In a historical résumé it was shown how very recent most prior inventions and discoveries were, and it was pointed out that a very large proportion of the inventions were made by American scientific men.

The many smokeless powders manufactured or prepared were then described or enumerated and classified into mixtures of different cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with nitroglycerol; mixtures of cellulose nitrates with nitro-substitution compounds; and pure cellulose nitrate powders; and the methods of manufacture were briefly stated.

The lecturer then related his own experience in inventing a smokeless powder. Recognizing at the outset the necessity for the closest approximation to absolute chemical and physical uniformity in a high-powered powder, and being familiar with the difficulty of securing such constancy in a physical mixture, he set about producing a powder from carefully purified cellulose nitrate of the highest degree of nitration. This was the first and only attempt made, so far as the lecturer was aware, to produce a powder which consisted of a single substance in its pure state.

A factory was erected at the Torpedo Station, prior to his resignation of his position there, and the powder manufactured was proved at Indian Head by Ordnance Officers of the Navy. Secretary Tracy said of this powder, "Report of the Secretary of the Navy, 1892, page 25." "It became apparent to the Department early in this administration that unless it was content to pass behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe." With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the Torpedo Station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto obtained in foreign countries."

The conditions that a smokeless powder should fulfill and the tests prescribed by the lecturer were then set forth, and in closing he pointed out that the powder was now developed to a higher degree than the gun and that changes in the latter to render it more efficient were being considered by ordnance experts.

CINCINNATI SECTION.

The Section met in regular session, Tuesday, March 17, 1896. President Twitchell presided.

The discussion of "The Scientific Concepts of Etidorhpa" was announced for the evening. The popularity of the book was evidenced by the presence of many friends of the author and of the other members of the Section.

Dr. Alfred Springer read extracts from the book and took issue with the author on some of the statements. Prof. Lloyd re-affirmed his belief in the theories advanced and referred the Doctor to the preface to the author's edition, in which he had stated he would decline "to make any subsequent comments on the work." The Professor then read three chapters in the original manuscript, which had been omitted from the published work. He now regrets the omission, as the continuity of the narrative is somewhat impaired thereby.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, April 16, 1896, Chairman, Charles A. Catlin, presiding.

Mr. Charles S. Bush read a paper on "Petroleum Products." The following is an outline of the paper:

1. Discovery of petroleum.
2. Brief history of the petroleum industry in the United States.
3. Outline of the distilling and refining process now in general use in the United States.
4. The importance of petroleum as a means of reducing friction to a minimum.
5. New methods compared with old ones, especially referring to "petroleum products" used for lubricating purposes.

NEBRASKA SECTION.

The regular meeting of the Nebraska Section was held at the University of Nebraska, on Tuesday evening, March 31, at eight o'clock.

The president being absent, Mr. Samuel Avery was elected chairman *pro tem.*, and called the meeting to order.

The following papers were read :

"Recent Work on the Röentgen Rays," by Prof. D. B. Brace, of the Department of Physics, University of Nebraska.

"Report on Argon," by Miss Rosa Bouton.

"Calcium Carbide and Acetylene," by Dr. John White.

Prof. Brace exhibited some Crookes' tubes prepared in his laboratory, made a general statement of the manner in which these were prepared and used, of the effect of the X or Röentgen rays, and exhibited some photographs taken by their use. Of these one was of special interest; it represented a shadograph of a metal object taken by the cathode and anode rays. There was no appreciable distinction between them.

Miss Bouton's paper gave a very thorough and clear account of argon, from the very earliest experiments of Lord Rayleigh on the density of nitrogen down to and including the present state of our knowledge of argon, its chemical and physical properties.

Dr. White exhibited a specimen of calcium carbide, which had been prepared in the electrical laboratory of the University, gave a brief historical statement of the carbides in general, and of their use in the preparation of acetylene. He then prepared some acetylene by treatment of the carbide with water, and by burning the gas under proper conditions showed how it may be used as an illuminant. He followed this by a short lecture, in which the economic use of acetylene as an illuminant was dealt with, laying special stress upon its advantages and disadvantages.

Owing to the lateness of the hour, Dr. White's paper on "Metallic Suboxides" was postponed.

At the business meeting which followed, Mr. E. C. Ellioet and Miss Marietta Gray were elected members of the Section.

NEW YORK SECTION.

Minutes of the meeting of April 10.

A report was made by the chairman of the committee appointed

to consider the organization of a chemical club in New York. Out of eighty-two replies already received, sixty were unconditionally in favor of the project.

It was further stated that as there had evidently been some misunderstanding as to the intended membership, it should be known that there is no intention of limiting the membership to any section of the chemical fraternity, but to include chemists and chemical manufacturers generally.

Dr. Albert R. Leads read a paper on "Standard Prisms in Water Analysis, and the Valuation of Color in Potable Waters."

In the discussion of Dr. Leed's paper, Prof. Birchmore explained an arrangement of adjustible colored prisms projecting inside a glass cylinder, one over the other, by which the Nessler reagent colors could be matched and recorded. The cylinder is to be filled with a liquid having the same refractive index as glass; oil of juniper was mentioned as suitable; and the record is made by readings on the milled heads of the screws by which the overlapping of the prisms is regulated.

Dr. Leeds moved that a committee be appointed to unify the methods of color comparison and report upon a standard of measurement of color in potable waters.

Prof. McMurtrie thought that such committee should be appointed by the council, and that the secretary should communicate the resolution to the President of the Society.

Dr. Leeds' motion, as amended by Prof. McMurtrie, was seconded and carried.

A paper was read by C. L. Speyers on "Matter and Energy."

Dr. E. G. Love exhibited some fine photomicrographs of starches.

Dr. L. Saarbach exhibited and described an improved form of "Laboratory Temperature Regulator," which he had found sensitive, reliable, adjustable, and easily taken apart for cleaning.

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HYDROFLUORIC ACID.[1]

BY KARL F. STAHL.

Received March 10, 1896.

HYDROFLUORIC acid is always made by decomposing ground fluorspar with sulphuric acid in cast iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing forty to fifty-two per cent. hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta percha bottles. Weaker acid, of about thirty-five per cent. and less, can be stored for a limited time in wood and is sometimes shipped in barrels, usually oil barrels. In this country the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting point of the ceresine is low. In Europe the C. P. acid is shipped either in gutta percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta percha and ceases to be C. P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:

1. *Hydrofluosilicic Acid.*—This is the most important impurity,

[1] Abstracted from a lecture before the chemical section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. Communicated by the author.

not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluorspar, which is all dissolved and volatilized by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluorspar contains usually about one and a half per cent.; samples of English spar, which I have tested, were even higher in silica, about three per cent., while six samples of German spar contained from one-tenth to seven-tenths per cent. silica. In the rapid determination of silica in fluorspar an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method:

One gram of ground fluorspar, in a platinum dish, with a small platinum spatula, is dried at about 130° C., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath; this is repeated, then dried again at 130° C., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates, for instance clay; in that case a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained and the silica be found too low. If carbonates are present the error would not be great, for instance,

$$CaCO_3\ (100) \text{ would give } CaF_2\ (78),$$

and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a grayish or bluish color, in that case

$$PbS\ (239) \text{ would give } PbF_2\ (245),$$

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

The great damage done by silica in the spar is plainly shown by the following equation:

$$(1)\quad \underset{60}{SiO_2} + \underset{234}{3CaF_2} + \underset{294}{3H_2SO_4} = \underset{144}{SiF_4(HF)_2} + \underset{408}{3CaSO_4} + \underset{36}{2H_2O}.$$

For every part of silica about four parts of fluorspar and five parts of sulphuric acid are wasted, or expressing it in money value, for every per cent. of silica at least ten per cent. (four per cent. for spar and about seven per cent. for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric Acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analyzing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The methed of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons, first, because the methods for determining the specific gravity of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it; picnometers are out of the question; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, *i. e.*, hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the

character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of 15° C., often remaining there for at least five minutes; the specific gravity is taken; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out:

1. Two grams in a very small platinum crucible (holding about five cc).

2. Two grams in a large platinum crucible (holding about forty cc.)

3. Four grams in a small platinum dish.

A. TOTAL ACIDITY.

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 cc.), then run, according to the expected percentage, twenty-five or fifty cc. normal caustic solution (forty grams caustic soda per liter) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add two drops of a solution of phenolphthalein (1 gram in 100 cc. alcohol) and then add more of the normal soda solution from a burette till the colorless liquid assumes the characteristic bright red color. Place over a Bunsen burner and heat to about 50° C; the red color will disappear. Finally add normal solution from the burette slowly till the red color remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralized. The number of cubic centimeters used we call "*a*."

If litmus is used in place of phenolphthalein, the soda solution has to be added till the color is perfectly blue, but the end of the

reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

B. HYDROFLUOSILICIC ACID.

To the acid in the large platinum crucible (two grams) add five cc. water (measured approximately), then slowly about two grams[1] potassium carbonate either in small pieces or in concentrated solution, add about fifteen cc. of fifty per cent. alcohol and then as many cubic centimeters of ninety-five per cent alcohol as water used, which will bring the whole to a volume of about twenty-five cc. containing about fifty per cent. alcohol,[2] let it stand for at least one hour. Filter[3] and wash the gelatinous precipitate, consisting of potassium silicofluoride, with fifty per cent. alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about twenty-five cc. of water and warm to about 50° C., titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of cubic centimeters used we call "*b*."

C. SULPHURIC ACID.

Place the platinum dish containing four grams of the acid to be tested, on a water-bath under a hood with a good draft and evaporate till acid fumes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of cubic centimeters used we call "*c*."

The reactions involved are as follows:

(2) $$\underset{20}{HF} + \underset{40}{NaOH} = \underset{42}{NaF} + \underset{18}{H_2O}.$$

[1] The amount of potassium carbonate is calculated to neutralize the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analyzing acid of entirely unknown composition I take for every cubic centimeter normal soda solution used for the determination of total acidity 0.05 gram potassium carbonate. Potassium chloride might be used in place of the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

[2] If the liquid contains more than fifty per cent. alcohol, potassium fluoride is precipitated, if much less alcohol, potassium silicofluoride may remain in solution.

[3] I use a platinum funnel because glass funnels are acted on, but that does not influence the accuracy of the method.

$$(3)\quad \underset{144}{SiF_4(HF)_2} + \underset{240}{6NaOH} = \underset{252}{6NaF} + \underset{60}{SiO_2} + \underset{72}{4H_2O}.$$

$$(4)\quad \underset{220}{SiF_4(KF)_2} + \underset{160}{4NaOH} = \underset{168}{4NaF} + \underset{116}{2KF} + \underset{60}{SiO_2} + \underset{36}{2H_2O}.$$

$$(5)\quad \underset{98}{H_2SO_4} + \underset{80}{2NaOH} = \underset{142}{Na_2SO_4} + \underset{36}{2H_2O}.$$

Now the number of cubic centimeters of normal soda solution used in the first titration and called "a" represents the alkali necessary to neutralize the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of cubic centimeters used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (two grams) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of cubic centimeters used, because in the potassium silicofluoride two atoms of fluorine are neutralized and we only neutralize with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required $b + \frac{b}{2}$ cc. to neutralize the free acid.

Having employed four grams of substance for the determination of the sulphuric acid, the number of cubic centimeters used for that determination must be divided by 2. The number of cubic centimeters used for hydrofluoric acid alone are therefore equal to $a - (\frac{3}{2}\, b + \frac{c}{2})$ and as each cubic centimeter normal solution indicates 0.020 gram HF and two grams of substance have been used, the number of cubic centimeters found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore

$$a - (\tfrac{3}{2}\, b + \tfrac{c}{2}) = \text{per cent. free hydrofluoric acid.}$$

After the foregoing explanation the calculation of the percentage of hydrofluoric acid is an easy matter. One cc. normal sodium hydroxide indicates 0.055 gram potassium silicofluoride, which was obtained from 0.036 fluosilicic acid; having used two grams of substance, 0.036 has to be divided by 2 and multiplied by 100 to get the percentage, or

$$b \times 1.8 = \text{per cent. hydrofluosilicic acid.}$$

The percentage of free sulphuric acid is obtained by multiplying c, the number of cubic centimeters used, by 0.048, dividing by 4 and multiplying by 100, or

$$c \times 1.2 = \text{per cent. free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid and their presence can easily be detected by well-known analytical methods:

To give an idea of the composition of some of the makes of hydrofluoric acid, I have appended a few of the analyses made in the course of five years:

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity.....	...	1.299	1.264	1.253	1.244	1.264	1.282	1.247	1.234
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrofluoric acid....	39.6	42.2	44.3	48.1	48.6	51.1	54.2	48.6	33.5
Hydrofluosilicic acid.	2.7	14.9	10.1	4.7	5.0	6.8	8.1	6.3	10.6
Free sulphuric acid..	...	0.8	0.8	4.0	1.9	1.4	1.2	0.8	1.6

1. Oct. 1891. Baker & Adamson, C. P. acid in ceresine bottle, 0.005 per cent. non-volatile residue.

2. Oct. 1891. Manufactured by J. C. Wiarda, sample received.

3. Nov. 1891. " " " " sample taken from package of 100 pounds.

4. Jan. 1892. Manufactured by James Irwin & Co., sample of lot of 3500 pounds.

5. Mar. 1892. Manufactured by James Irwin & Co., sample of lot of 3400 pounds.

6. Jan. 1894. Manufactured by Bender & Aldred, sample taken from package of 100 pounds.

7. Jan. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3000 pounds.

8. Oct. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3200 pounds, 0.015 per cent. non-volatile residue.

9. Jan. 1896. So-called "pickling acid" sample received from a foundry.

By comparing analyses Nos. 2 and 7 it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains twelve per cent. less hydrofluoric acid, but six and eight-tenths per cent. more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains six and eight-tenths per cent more hydrofluoric acid and three and there-

tenths per cent. less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time, most extensive application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluorspar and sulphuric acid. This is the oldest way of etching and I believe most burettes, graduated cylinders, etc., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulas are published and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, etc., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque goes under the trade name of

"white acid." Lead glass is very rapidly and uniformly etched and acid of forty-five to forty-eight per cent. is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as fifty-two per cent. HF is employed. "White acid" is much more convenient for application than gaseous acid and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass, even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about 15° C. Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle work a mixture of Burgundy pitch and beeswax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means, or with sulphuric acid, but the first is expensive and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings, which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about one or two per cent. HF, the pickling can therefore be carried on in wooden vessels.

Some of the firms, who use hydrofluoric acid for cleaning iron, have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission:

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes:

"We use the acid in the proportion of two and one-half quarts to one-half barrel water, containing about twenty-five gallons," —(equal to one pound forty-eight per cent. hydrofluoric acid

in thirty-five pounds of water, the liquid would therefore contain one and four tenths per cent. HF)—" The bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

" We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings."—(as the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of ninety-three per cent. sulphuric acid in eleven pounds of water, the liquid would therefore contain eight and a half per cent. sulphuric acid, or six times as much as the hydrofluoric acid bath.)

" With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint, with which the castings were subsequently covered.

" We had no occasion to try this acid for cleaning any other material but cast iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast iron and wrought iron. The hydrofluoric acid did this to perfection and left a perfectly bright surface.

" I can say, in conclusion, that I am perfectly satisfied, that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid."

From the engineer of another firm I received the following report:

" The best solution is one to thirty" —(this is by volume, and the bath would contain, as he used forty-eight per cent. hydrofluoric acid about two per cent. HF)—" As we make no small castings of gray iron I have only used the acid on maleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of one acid to fifty water"—(the bath would contain about one per

cent. HF)—"by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

"It takes sulphuric acid twice as long with the same proportion"—(that is, one to thirty would give a solution of about five and six-tenths per cent. sulphuric acid)—"and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron and does not leave it bright."

For iron which is to be enameled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning sixty tons a day.

Hydrofluoric acid or its salts are also used in distilleries to insure a more complete fermentation.[1]

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is dryer after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

NITROGEN ASSIMILATION IN THE COTTON PLANT.

BY CHARLES E. COATES AND W. R. DODSON.

Received March 3, 1896.

IN the spring of 1895, while looking up the literature of the cotton plant, it was noted that no quantitative work could be found touching the question of nitrogen assimilation in any member of the mallow family. As the cotton plant is highly nitrogenous in character and as there seemed to be no reason why the leguminoseae should have a prëemption claim on the absorption of free nitrogen, it was decided to undertake certain experiments along these lines, following Hellriegel's methods as far as possible, in the hope that something of importance might

[1] Article of Dr. Leo Backeland, this Journal, 14, 212.

be discovered concerning the relationships of cotton to atmospheric nitrogen. The conclusions of these experiments, however, were so entirely negative that this hope has been abandoned, and while, perhaps, they have not disproved the point in question absolutely, still it has been decided to put them on record in the belief that they afford at least strong evidence that cotton does not follow the legumes in this respect.

The method of work was as follows: A quantity of white sand was sifted through a one and a half mm. sieve, heated red hot in an iron pan and washed first with ordinary artesian water and afterwards with nitrogen-free water. Ten grams gave no nitrogen when analyzed by the usual Kjeldahl method. Ordinary flower pots were used, holding each about six pounds of sand. The sand had a water-holding capacity of about twenty-three per cent. It was kept moist to the extent of about seventy-five per cent. of its maximum capacity. The water used was obtained from artesian water nearly free from ammonia by distilling it and collecting only the middle third of the distillate. It gave merely traces of ammonia with Nessler's solution when analyzed in the usual way. A number of cotton seeds were linted as thoroughly as possible. The average weight of fifty-one seeds was 0.1166 gram. Of these, thirty-eight were weighed accurately and the weights of twenty fell between 0.110 gram and 0.130 gram. These twenty were soaked twenty-four hours in pure water, placed on moist sand in a dish, covered with a piece of filter paper, and the dish covered with a glass plate. As soon as a normal germ and rootlets appeared the seeds were planted in the pots, only those seeds being selected which showed about the same germinative energy. Before planting, four cc. of each of the following solutions were added to certain pots: potassium phosphate, 136 grams to liter; magnesium sulphate, 120 grams to liter; potassium chloride, 74.5 grams to liter; and calcium chloride, 70.8 grams to liter. The seeds were planted about three-quarters of an inch deep in the sand and the pots were covered with cotton wadding until the plant appeared. They were kept in the open air and put under cover whenever it threatened rain. On one occasion a small quantity of rain fell on the pots. Otherwise they received only nitrogen-

free water. The seeds were all planted on the first of May.

Pot 1.—No nutriment was added to this pot. The plant was dead by May 18.

Pot 2.—Same as 1. The plant was dead by May 28th.

The growths were so little in 1 and 2 that no analyses were made. To 3, 4, 5, 6, and 7 the solutions mentioned before were added. They were mixed, diluted to about 500 cc., mixed thoroughly with the sand in a porcelain dish and transferred to the pot before the seed was planted. After the plants had been growing a week or so, to 5, 6, and 7 there were added twenty-five cc. of a soil infusion, made as follows: A quantity of earth was taken from a field which had been planted in cotton for ten or twelve years. This earth was mixed thoroughly and 200 grams were shaken with one liter of water. After standing an hour or so, the clear supernatant liquid was decanted. A nitrogen determination gave 0.0002 gram nitrogen to twenty-five cc. of this liquid. It was applied by a pipette to the roots of the plant while in the pot. The assumption was that any bacterial agencies which might affect the cotton plant would surely be present in the soil of the old cotton field. A similar method had proved efficacious in innoculating legumes.

Pot 3.—With mineral food—without soil infusion. The plant died about the last of May, apparently of nitrogen starvation.

Pot 4.—Same as 3. The plant lived until the close of June, but growth had ceased by June 15. June 27 this plant and plants 5, 6, and 7, were removed from the pots and analyzed as follows: The sand was washed carefully from the roots, the entire plant was dried at 100°, and the nitrogen determined by the Kjeldahl method. In this case the seed weighed 0.1300 gram. A series of analyses had given 3.07 per cent. nitrogen in the whole cotton seed.

	Gram.
Nitrogen in seed of 4	0.004
Dry matter in seed of 4	0.5050
Nitrogen found in seed of 4	0.0068

Pot 5.—With mineral food, plus soil infusion.

	Gram.
Seed weighed	0.1244
In seed nitrogen	0.0038
Dry matter	0.4768
Nitrogen found	0.0056

Pot 6.—Same as 5.

	Gram.
Seed weighed	0.1285
In seed nitrogen	0.0039
Dry matter	0.8350
Nitrogen found	0.0074

Pot 7.—Same as 5 and 6.

	Gram.
Seed weighed	0.1175
In seed nitrogen	0.0036
Dry matter	0.9664
Nitrogen found	0.0080

In all these instances growth had stopped before the plants were removed from the pot. The gain in nitrogen without soil infusion was 0.0028 gram; with soil infusion, 0.0018, 0.0035, and 0.0044 gram. Apparently it mattered very little whether the soil infusion was added or not and in all the instances the gain was so inconsiderable as to lie well within the limits of error of the experiments. It would seem therefore that under the conditions employed the cotton plant does not assimilate atmospheric nitrogen.

CHEMICAL LABORATORY,
LOUISIANA STATE UNIVERSITY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 19.]

DETERMINATION OF LACTOSE IN MILKS BY DOUBLE DILUTION AND POLARIZATION.

BY H. W. WILEY AND E. E. EWELL.

Received March 20, 1896.

IN volume 6, page 289, of the *American Chemical Journal*, one of us (Wiley) published an article on the determination of lactose in milks by optical methods. The principal novelty in this process was the substitution of mercuric nitrate as the reagent for precipitating proteids in place of the other reagents which had usually been employed for that purpose. By the use of mercuric nitrate in an acid solution, it was shown in that

paper that it was possible to practically throw out all of the proteid dissolved in the milk. Inasmuch as these soluble proteids are optically active, and deflect the plane of polarization in a direction opposite to that produced by lactose, the presence of any notable quantity of them in the solution to be polarized tends to diminish the apparent percentage of lactose present. The reagent proposed, *viz.*, acid mercuric nitrate, when used in the cold and in the quantities specified, produces no inversion effect whatever upon the lactose.

In the paper referred to an arbitrary correction was made for the volume of the precipitate produced and this was fixed at two and five-tenths cc., when approximately sixty cc. of milk were used in a 100 cc. flask.

This method of estimating lactose on account of the ease with which it can be operated and its accuracy has been generally adopted by chemists. Attention has been called, however, to the fact that the arbitrary correction allowed for the volume of the precipitate is too small.[1]

Theoretically, it is evident also that the arbitrary correction admitted is too small except in cases of well-skimmed milk. In order to eliminate this arbitrary factor from the method, we undertook a series of experiments to determine the actual percentage of sugar and the proper correction to be allowed for the volume of the precipitate by the method of double dilution and polarization originally proposed by Scheibler for sugar solutions, and suggested by Bigelow and McElroy for use in the polarization of milk sugar.[2] The results of our determinations are extremely satisfactory, and show that the volume which is occupied by the precipitate in a milk varies from two and a half cc,, in the circumstances mentioned above, to six cc., according to the richness of the milk in fat. It appears, however, that this correction is less in quantity than the apparent combined volume of the fat and albuminoids which may be safely assumed to be one cc. for one gram.

All the flasks which were employed in the determinations were carefully calibrated, and the instrument used was the new triple-field shadow polariscope, made by Schmidt and

[1] *Analyst*, 12, 64; 20, 126.

[2] This Journal, 15, 694.

Haensch, which enables readings to be accurately made to within 0.05 per cent. All readings were made in duplicate by each of us and entered before comparisons were made, and in the polarizations given in the table the means of these four readings, which never differed by more than one-tenth per cent., are given. The polarizations were made on the contents of a 100 and a 200 cc, flask, after clarification of the milk by means of acid mercuric nitrate. In each case, double the quantity of the normal weight of milk for the instrument used was taken. The readings were calculated by the formula given by Scheibler, which requires that the reading obtained from the solution in the large flask be multiplied by two and subtracted from the reading obtained in the small flask. In all cases, in order to secure greater accuracy, our readings were made in a tube 400 mm. in length. Therefore, the data obtained in reading the solution in the small flask were divided by four in order to obtain the apparent percentage of sucrose.

The application of the formula given by Scheibler does not give absolutely accurate results. The true polarization in any given case is calculated according to the following scheme:

Let x equal the volume of the precipitate and y the correct reading. Let a equal the reading obtained from the solution in the small flask and b equal the reading of the solution from the large flask. We then have

$$200 - x : 100 - x :: a : b$$

$$200\,b - bx = 100\,a - ax$$

$$ax - bx = 100\,a - 200\,b$$

$$x = 100\,\frac{(a - 2b)}{a - b} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$100 - x : 100 :: y : a$$

$$100 - 100\,\frac{(a - 2b)}{a - b} : 100 :: y : a$$

$$100\left(a - \frac{a\,(a - 2\,b)}{a - b}\right) = 100\,y$$

$$y = a - \frac{a\,(a - 2b)}{a - b}$$

$$y = \frac{a^2 - ab - a^2 + 2ab}{a - b} = \frac{ab}{a - b} \qquad \ldots\ldots\ldots (2)$$

The rule derived from formula No. 2 is as follows:

The true polarization, as determined by double dilution, is found by dividing the product of the two readings made from the solutions in the large and small flasks by their difference.

In order to test the accuracy of the method, known volumes of insoluble material, as, for instance, quartz sand, were added to the flasks in order that the volume of the precipitate might be increased by a certain definite amount. The determinations were also made on the whole milk as purchased, on the same milk deprived of the most of its cream and on the cream thus secured. In all cases the results obtained were perfectly satisfactory.

Blyth has lately described a method of precipitating the casein with acid and of washing the precipitate free of sugar on a filter and polarizing the filtrate.[1] The percentage of milk sugar in the mixed filtrate and washings is about one and the polariscopic reading should be corrected for that degree of dilution. This method evidently is better suited for preparing milk whey for the gravimetric estimation of the sugar by copper, since it takes no account of the albumens still in solution and serving to a certain extent to counteract the polarizing power of the lactose.

In the presence of sucrose he proposes to estimate its quantity from the property possessed by citric acid of inverting the sucrose and leaving the lactose unchanged. Raumer and Späth[2] suggest that the polarization of milk should be preceded by boiling, since it is probable that the lactose may exhibit birotation. The data which they adduce, however, are far from convincing, since after the boiling they clear the mixture with lead subacetate and it has been shown that this reagent does not remove all the proteids. The deficit in rotation is therefore probably due to the residual soluble left-handed proteids. They further suggest that the presence of a dextrinoid body, as indicated by Ritthausen[3] may serve to increase the actual rotation of the milk sugar. In the samples which showed the apparent

[1] *Analyst*, 20, 122.
[2] *Ztschr. angew. Chem.*, *1896*, 72.
[3] *J. prakt. Chem.* (2), 15, 348.

increase, however, they made no attempt to prove the presence of the alleged disturbing dextrin.

There seems to be no just reason, therefore, for insisting on the slow and tedious gravimetric method when a quick and accurate optical method is at hand.

Inasmuch as the time required for carrying out the method of double dilution and polarization is scarcely any longer than that required for a single polarization, it is recommended that it be done in all cases, instead of correcting the results of a single polarization by any arbitrary factor. When the determination is conducted as suggested, the analyst has at hand an easy, rapid, and accurate method of estimating milk sugar in milk, which is as desirable in all respects as any gravimetric method whatever. The data obtained are given in the accompanying table.

POLARIZATION OF MILK BY DOUBLE DILUTION.

No.	Per cent. fat.	Polarization in 200 cc. flask.	Polarization in 100 cc. flask.	Apparent per cent. lactose.	True per cent. lactose.	True volume in 100 cc. flask.	Volume of precipitate.
1	....	9.37	19.26	4.82	4.56	94.4	5.6[1]
2	....	9.59	20.33	5.08	4.54	88.8	11.6[2]
3	....	9.36	19.20	4.80	4.57	95.0	5.0[3]
4	....	9.60	20.25	5.06	4.56	89.7	10.3[4]
5	2.9	10.15	20.84	5.21	4.95	94.8	5.2
6	4.8	10.31	21.21	5.30	5.00	94.5	5.5
7	3.1	9.49	19.41	4.85	4.64	95.7	4.3[5]
8	4.0	10.01	20.45	5.11	4.90	95.9	4.1
9	1.4	9.44	19.26	4.82	4.63	96.1	3.9[6]
10	5.5	11.05	22.68	5.67	5.38	94.8	5.2
11	4.4	9.57	19.47	4.87	4.71	96.5	3.5[7]
12	2.0	9.75	19.93	4.98	4.77	95.8	4.2[8]
13	17.6	8.72	19.13	4.78	4.01	82.4	17.6[9]

Summary of Method.—For the scale of the instrument used, 32.91 grams of pure lactose in 100 cc. give a reading of 100. This number is derived from the following data: For sucrose concentration twenty-five grams in 100 cc., $[\alpha]_D^{20°}=66.37$.

1 Without sand.
2 With five cc. quartz sand.
3 Without sand.
4 With five cc. quartz sand.
5 Same as No. 6, after separation of cream.
6 Same as No. 8, after separation of cream.
7 Whole milk.
8 Skimmed milk.
9 Cream.

For lactose, thirty-three grams in 100 cc., $[\alpha]_D^{20} = 52.53.$; then $66.37 : 52.53 :: x : 26.048$, whence $x = 32.91$. The temperature of the working room should be kept at about 20°, since the rotatory power of lactose diminishes in a small degree as the temperature rises. Double the quantity mentioned, *viz*,, 65.82 grams of milk are placed in a 100 cc. flask, clarified with mercuric nitrate solution, the volume completed to the mark, the contents of the flask well shaken, poured upon a filter, and the filtrate polarized in a 400 mm. tube. A similar quantity of the milk is placed in a 200 cc. flask and subjected to the same treatment. The polarimetric data obtained are used for calculating the true volume of liquid in the flask and the true percentage of lactose and the true volume occupied by the precipitate, in accordance with the rule already given, or with sufficient accuracy by Scheibler's formula. The acid mercuric nitrate solution is prepared as follows:

Dissolve mercury in double its weight of nitric acid, specific gravity 1.42, and add to the solution five volumes of water. This solution is more dilute than the one recommended in the original paper, it having been noticed that a stronger solution colors the precipitated proteid matter slightly yellow (xanthoproteic reaction). Ten cc. of the reagent are to be employed instead of two, as directed for the stronger solution. In preparing the solution of milk in the 200 cc. flask it may be necessary at times to use more than this quantity of the acid mercuric nitrate in order to secure a filtrate entirely free of turbidity.

An inspection of the data in the table shows a general agreement between the volume of the precipitate found and the percentage of fat in the sample with the exception of one instance, *viz.*, No. 11. It is evident that in solutions so dilute, a slight variation in the volume has a very small influence on the percentage of sugar found. An error of 0.05 degree in the reading of the dilute solution (200 cc. flask) makes an error of 0.05 per cent. in the result. The error due to one cc. of the precipitate in the dilute solution is approximately 0.05 per cent. It is therefore evident that with proper care the percentage of sugar can be determined to within one-tenth per cent. by the polarimetric method and this is entirely sufficient for all practical purposes.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM. No. 5.]

A STUDY OF THE ZIRCONATES.

BY F. P. VENABLE AND THOMAS CLARKE.

Received March 6, 1896.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.[1] Of recent years several papers by L. Ouvrard[2] have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the Jahresberichte, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watt and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof

[1] *Ann. Chem. Pharm.*, **137**, 34, 236.

[2] *Compt. Rend.*, **112**, 1444-46, and **113**, 1021-22.

that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it: ZrO_2, 78.54 per cent.; Na_2O, 5.40 per cent.; and H_2O, 16.89 per cent., corresponding to $Na_2O.8ZrO_2$. He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).

II. Fusing zirconia with alkaline carbonates, (Hiortdahl).

III. Fusing zirconia with alkaline hydroxides.

IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his ziconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninety-

three to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this $ZrO_2 = 75.70$ per cent.; $Na_2O = 24.30$.

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages: ZrO_2, 74.18; Na_2O, 25.81. These correspond fairly with $(ZrO_2)_3(Na_2O)_2$.

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages: ZrO_2, 58.16; Na_2O, 41.84.

II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. FUSION OF ZIRCONIA WITH HYDROXIDES.

1. Fusion with sodium hydroxide.

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved 1.1855 grams. An analysis, reduced to dry basis, gave ZrO_2, 92.29, and Na_2O, 7.65.

2. Same amount taken as in Experiment 1. Total amount dissolved 0.7655 gram, containing ZrO_2, 93.19, and Na_2O, 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing ZrO_2, 92.57, and Na_2O, 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent. ZrO_2.

$Na_2O.(ZrO_2)_6$ contains ZrO_2, 92.20; and Na_2O, 7.80.

$Na_2O.(ZrO_2)_7$ contains ZrO_2, 93.29; and Na_2O, 6.76.

2. Fusion with potassium hydroxide.

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent. ZrO_2.

2. Dissolved 1.5241 grams which contained ZrO_2, 82.98; K_2O, 17.00.

3. Dissolved 1.2078 grams which contained ZrO_2, 78.59; K_2O, 21.40.

4. Dissolved 0.9297 gram which contained ZrO_2, 85.51; K_2O, 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2, 93.51, and Na_2O, 6.49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it can not be claimed from the analyses that definite zirconates have been pre-

pared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(Na_2O)_2(ZrO_2)_3$. In the fusion with sodium hydroxide the results range from $(Na_2O)(ZrO)_5$ [$ZrO_2 = 90.76$; $Na_2O = 9.24$], to $(Na_2O)(ZrO)_8$ [$ZrO_2 = 94.08$; $Na_2O = 5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(K_2O)(ZrO_2)_3$ [$ZrO_2 = 79.57$; $K_2O = 20.43$], to $(ZrO_2)_5(K_2O)$, [$ZrO_2 = 86.74$; $K_2O = 13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2, 78.59 per cent., and K_2O, 21.41 per cent. was left. This nearly corresponds to the formula $K_2O.(ZrO_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2, 89.11 per cent.; Li_2O, 10.99 per cent. Percentage of ZrO_2 calculated for $Li_2O.2ZrO_2$ is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $CaO.ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.46

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result:

	Found.	Calculated for $BaO.ZrO_2$.
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained:

	Found.	Calculated for $SrOZrO_2$.
ZrO_2	54.22	54.55
SrO	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams) was heated together for about four hours and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found.	Calculated for $MgO.ZrO_2$.
ZrO_2	76.28	75.30
MgO	23.70	24.70

IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3.

1. Fusion with sodium chloride.

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

2. Fusion with potassium chloride.

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. Fusion with alkaline earths.

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths except where these chlorides are

decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing; especially as somewhat similar experiments were carried out under the next heading.

VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50 per cent solution potassium hydroxide dissolved per cc.								0.00233	gram.
33	"	"	"	"	"	"	"	0.00097	"
25	"	"	"	"	"	"	"	0.00075	"
12	"	"	"	"	"	"	"	0.00009	"

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc. 0.00245 gram.
25 " " " " " " 0.0012 "
12 " " " " " " 0.0005 "

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of the water during the washing, but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as CaO.ZrO, etc. The same is true of the magnesium compound. For lithium the compound obtained was LiO.ZrO. For the alkalies it seemed to be possible to ob-

tain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

1. Potassium calcium zirconate.

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave ZrO_2, 67.21 per cent.; CaO, 31.06; K_2O, 1.11. This is a calcium zirconate, ($CaO.ZrO_2$), with a small part of the CaO substituted by K_2O.

2. Potassium aluminum zirconate.

Two grams of zirconia were fused for eight hours with two grams of potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave ZrO_2, 72.38 per cent.; Al_2O_3, 7.66; K_2O, 20.00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.

UNIVERSITY OF NORTH CAROLINA.

A MODIFIED AMMONIUM MOLYBDATE SOLUTION.

By A. L. Winton.

Received March 18, 1896.

WHEN phosphoric acid is determined by the molybdate method, it is a common practice to add fifteen grams of ammonium nitrate to the phosphate solution and heat before adding ammonium molybdate. By this means the separation of the yellow precipitate is greatly facilitated and the time of digestion shortened. But to dissolve this nitrate requires some time and very greatly reduces the temperature of the solution so that special care is necessary in heating it subsequently. In the laboratory of this station it has been our practice to simplify the process by omitting the separate addition of ammonium nitrate and using a molybdic solution containing the requisite quantity of the salt. Such a solution may be prepared according to the following formula:

I. Dissolve 1000 grams of molybdic acid in 4160 cc. of a mixture of one part of concentrated ammonia water (sp. gr. 0.90) and two of water.

II. Dissolve 5300 grams of ammonium nitrate in a mixture of 6250 cc. of concentrated nitric acid (sp. gr. 1.4) and 3090 cc. of water.

Add I to II slowly with constant stirring. Allow to stand for a few days in a warm place and decant off the clear liquid.

This solution has the same proportion of ammonium molybdate and free nitric acid as the molybdic solution of Fresenius, but differs from the latter in that *fifty cc. contain fifteen grams more of ammonium nitrate*. We have prepared the solution so as to contain this proportion of the salt because in the routine analysis of fertilizers in the station laboratory fifty cc. are most commonly employed. This quantity in our experience is usually sufficient for the precipitation of the soluble, insoluble or total phosphoric acid of mixed fertilizers in solutions representing four-tenths, two, and five-tenths grams respectively of the material.

In no case ought less than fifty cc. be used, for otherwise there may not be enough ammonium nitrate present for the perfect separation of the yellow precipitate. When a larger quan-

tity of molybdic solution is required, as, for example, in the determination of total phosphoric acid in ground bone, bone black, Thomas slag, etc., it may be added without fear that the larger quantity of ammonium nitrate contained in it will in any way interfere with the process. If, however, it is thought desirable, a special molybdic solution containing fifteen grams of added ammonium nitrate to every seventy-five or 100 cc. of the liquid may be prepared for such cases.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN, CONN.

ON THE ESTIMATION OF SULPHUR IN PYRITES.

BY THOMAS S. GLADDING.

Received March 30, 1896.

IN the October (1895) number of this Journal, Dr. Lunge continues his discussion of the estimation of sulphur in pyrites. He presents no new experimental support of his position. He indirectly accuses me of having published a "private" communication without the sanction of the writer, Prof. Richards. In reply I will say that the words of Prof. Richards were published by myself, not only with full permission, but after a careful revision of the same by their author. Had Dr. Lunge addressed a note to Prof. Richards or to myself, he would have been saved from making a most unkind and needless accusation.

While Lunge attempts no further support of his position by chemical experiment, he makes the claim that any occlusion of barium chloride that occurs is compensated for by the solubility of barium sulphate in the acid liquor of precipitation. In his own words "my claim has been that my method by compensation of unavoidable errors, gives *correct results*."

I have investigated this claim of Lunge's, as far as it applies to the occlusion of barium chloride in his method, in the following manner: I have had one of our assistants repeat the work with chemically pure sulphate of ammonia, using two grams in each case, making comparison precipitations with a ten per cent. solution of barium chloride, the first by adding the barium chloride solution drop by drop from a burette, the second by sudden addition from a small beaker in which it had been brought to the boiling point. The results were as follows:

	By slow addition. Gram.	By sudden addition Gram.
Sulphur	0.4840	0.4880
Sulphur	0.4820	0.4873

These experiments show an occlusion of about 0.040 gram barium chloride and a corresponding error of 0.50 to 0.55 per cent. in the estimation of the sulphur present.

I repeated personally the second series of precipitations obtaining:

	Barium sulphate obtained. Grams.	Sulphur. Gram.
1	3.5480	0.4878
2	3.5430	0.4871

These experiments show an error of about 0.55 per cent. in the estimation of sulphur present. The greatest care was taken in washing these precipitates. Three washings by decantation, using seventy-five cc. of hot water each time, were followed by five washings on the filter paper.

I now fused these precipitates with chemically pure sodium carbonate, dissolved the flux in water, filtered from barium carbonate, acidified the filtrate with nitric acid, added silver nitrate and from the silver chloride obtained, calculated the equivalent of barium chloride. I obtained in one case 0.0552 gram silver chloride, corresponding to 0.040 gram barium chloride, in the other 0.0500 gram silver chloride, equivalent to 0.0364 gram barium chloride. Deducting these figures, we have:

$BaSO_4$	3.5480	3.5430
$BaCl_2$	0.0400	0.0364
Pure $BaSO_4$ obtained	3.5080	3.5066

The sulphur obtained from these corrected results are 0.4823 gram and 0.4821 gram. These corrected results agree very closely with those obtained by our assistant when using the dropping method. I now fused one of the precipitates obtained by the dropping method with sodium carbonate in the same way and obtained 0.0027 gram silver chloride, equivalent to 0.002 gram barium chloride. This shows that the occlusion of barium chloride is practically avoided by adding the barium chloride drop by drop, as 0.002 gram barium chloride would cause an error of only 0.026 per cent. in sulphur.

I now took up the question of the solubility of barium sulphate in the acid liquor of precipitation, imitating the conditions under which the actual analysis of pyrites is made. To 400 cc. water were added fifteen cc. strong ammonia. Hydrochloric acid was now added to acidify. To two such preparations I added 0.020 gram and 0.040 gram chemically pure ammonium sulphate, respectively. The solutions were brought to the boiling point and ten cc. barium chloride added. The liquid was boiled till clear and allowed to settle. I obtained :

	Barium sulphate. Gram.	Sulphur obtained. Gram.	Sulphur present. Gram.
1	0.034	0.00468	0.00484
2	0.069	0.00949	0.00969

The sulphur lost by the solubility of the barium sulphate in the acid solution in the above experiments amounts to 0.016 and 0.020 per cent. respectively.

The above work demonstrates conclusively that the method employed by Lunge of adding the barium chloride all at once causes an error of about five-tenths per cent. in the percentage of sulphur, and that such error is *not* compensated for by the solubility of barium sulphate in the liquor of precipitation, as such solubility is very slight, causing an error of less than 0.03 per cent.

In his first reply (March, 1895), Dr. Lunge objected to my method of estimating the 0.20 to 0.40 per cent. of sulphur, (that may be left in the ferric hydroxide), by the simple process of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium sulphate solution and letting stand over night. This he declared was wrong, owing to the solubility of barium sulphate in such solution. I showed by a few simple and rigid experiments that I was entirely right. These experiments were very easily capable of repetition. But Lunge did not choose to repeat them. The above experiments showing that the sudden addition of barium chloride will cause an error of several tenths of a per cent. are likewise very easily repeated and the separation of the occluded barium chloride as described, is so positive as to the error caused by Lunge's method of procedure, that I hope for a further answer from Dr. Lunge. On account

of the commercial importance of an accurate estimation of sulphur in pyrites, I have no doubt that a prompt repetition of my work as described above will soon be published by some other analyst, and the main point at issue, namely, the necessity of a very slow addition of the barium chloride solution, be settled.

FURTHER NOTES UPON THE FATS CONTAINED IN THE TUBERCULOSIS BACILLI.

By E. A. de Schweinitz and Marion Dorset.

Received March 28, 1896.

In the *Journal of the American Chemical Society*, for August, 1895, we published an article upon the composition of the tuberculosis and glanders bacilli, and noted the probable composition of the fats which are present in these germs in considerable proportion. The amount of crude fat in the tuberculosis bacilli is very large, having been found by us to be in round numbers thirty-seven per cent. of the weight of the dried germs. In the article referred to the amount of fat at our disposal was very small, and we could at that time determine only palmitic acid, and a high melting acid, which we stated appeared to be arachidic so far as the quantity at hand could be utilized. Recently we have made some further study upon these fats, and the results so far obtained seem to be of sufficient interest to warrant publication as a continuation of our previous work.

The quantity of crude fat available, which had been extracted from the germs was about three and five-tenths grams, and this was examined in the following way: It was first saponified in a closed flask with sodium hydroxide, in accordance with the method prescribed, for the determination of fats by the American Association of Official Agricultural Chemists, as this method seemed to give the most satisfactory results. The saponification yielded a hard soap which was difficultly soluble in water. The dissolved soap was acidified with sulphuric acid and submitted to distillation until 100 cc. of the distillate had been obtained, again in accordance with the usually prescribed method. The distillate had a pungent odor, something like that of sweet almonds, and when titrated with tenth normal hydroxide

solution, required for neutralization two and four-tenths cc. of the latter. The total amount of volatile fatty acid was therefore exceedingly small. As the total amount of sodium hydroxide required to neutralize the volatile acid from three and five-tenths grams fat was only 0.0096 gram, the total quantity of volatile acid could probably not have been 0.05 gram, an amount too small to permit of a determination of its character.

The non-volatile fatty acids which formed a hard layer in the distilling flask were filtered off and well washed with water to remove all sulphuric acids and salts. The mixture was partially soluble in cold ninety-five per cent. alcohol, but readily soluble in hot absolute alcohol. The only method that appeared practical for the separation of the fatty acids in this mixture, was a fractional crystallization. Even this was extremely troublesome, but finally by repeated efforts the larger portion of the acid was found to have a melting-point of 62° C., which remained constant upon recrystallization. The principal fatty acid was therefore palmitic. After the palmitic acid had been removed a residue remained which was partially soluble in cold eighty-five per cent. alcohol, and partially in hot eighty-five per cent. alcohol. The acid soluble in hot eighty-five per cent. alcohol after the first crystallization melted at 85° C., while two subsequent crystallizations raised the melting point to 102° C. Unfortunately again the quantity of this high melting acid was too small for further crystallization or identification. It was evidently the same acid that in our first article we noted as probably arachidic acid.

The acid soluble in cold eighty-five per cent. alcohol was further purified and gave white crystals that melted at 42°–43° C., which would correspond to lauric acid. The amount was too small to permit of a positive identification.

This examination of the tuberculosis fats has shown that it is principally a glyceride of palmitic acid. In addition there is a minute amount of the glyceride of a volatile fatty acid to which the tuberculosis cultures owe their characteristic odor, and very small amounts of probably lauric acid and an unusually high melting acid, an acid apparently with a larger carbon content, so far as we can find, than any before noted in plants.

We propose still to identify the volatile and non-volatile acids found in such small quantities, but as it will require probably several years to collect the material for this work, it has seemed best to give the results so far obtained at the present time.

THE CASSEL-HINMAN GOLD AND BROMINE PROCESS.

By Parker C. McIlhiney.

Received March 24, 1896.

THIS process, recently introduced by the Gold & Bromine Co., is for the extraction of gold from low grade ores, and those which will not give up their gold to amalgamation. If an ore is free milling no process yet devised can compete with amalgamation for its treatment, and if it is of sufficiently high grade to bear transportation and smelting charges, and contains nothing to interfere with the process of smelting, there is comparatively little inducement to use a wet process. But for ores such as the telluride ores of Colorado, which will not amalgamate, and in which the gold and tellurium compounds are of such a friable nature that they cannot be concentrated, and which are in addition of too low grade to smelt, some wet process must be used. The wet processes which have proved commercially successful are chlorination and the cyanide process. Of the cyanide process nothing need be said except that on many ores it has been used very successfully and from many others it fails to extract a sufficiently high percentage of the gold present. Chlorination has, after being the subject of a great deal of experimenting, been reduced practically to two methods of operation: the vat process, in which the ore is treated with chlorine gas and water, without agitation, and the Thies barrel process, in which the ore is agitated in a revolving barrel with water, bleaching powder, and oil of vitrol. Of the two the barrel process is more generally applicable as the ore cannot be leached in vats unless it is comparatively free from slime and allows the liquid to pass through it readily. The barrel process is recognized generally as better practice. It is evident that in the vat process the strongest solution of chlorine which can at any time be in contact with the ore will be an aqueous solution saturated at the ordinary temperature and pressure, because it

is impracticable to place the vats under pressure. In the barrel process it has also been found impracticable, on account of mechanical difficulties, to treat the ore with chlorine under any considerable pressure, and, therefore, in the Thies process the strength of the chlorine solution is almost as limited as in the vat process, and moreover it has been found impracticable to introduce the chlorine in the Thies process as free chlorine, and it is now made entirely by means of bleaching powder and oil of vitriol, introduced with the ore. In order to effect the solution of the gold in the ore in a reasonably short time it is not sufficient to introduce a *small* excess of chlorine but a very large excess must be used to so hasten the solution as to bring the time within permissible limits. This excess of chlorine goes to waste, and although very many attempts have been made to recover it, none have ever proved practicable. The only safe way to get the gold out is to use as large an excess of chlorine as possible, and as the solubility of chlorine in water prevents the use of more than a small amount, it sometimes happens, even with careful working, that the ore being improperly roasted no gold is obtained at all.

As a substitute for chlorine, bromine has been used by many experimenters, and its use has been attempted in mills by a simple substitution of bromine for chlorine. But as bromine is very expensive its use without recovery has not been successful.

The properties of the two halogens, as far as concerns their use on ores, are about as follows :

Bromine is, at ordinary temperature, a liquid, boiling at 63° C., and which may be easily liquified again by a condenser supplied with cold water.

Chlorine is a gas which must, according to Nieman,[1] be placed under a pressure of six atmospheres at 0° C. in order to liquefy it, or cooled to —35° C. to condense it without pressure.

Bromine is soluble in water at 15° C. to the extent of three and two tenths per cent; this means about 25.5 pounds in 100 gallons of water.

Chlorine is soluble in water to the extent of about 0.76 per

[1] Brandes Arch., 36, 18 ; Dammer, Handb. Anorg. Chem., 1, 474.

cent. at 15° C.; this means about six pounds in 100 gallons of water.

Bromine is a much less powerful oxidizing agent than chlorine, and, as a result of this fact, oxidizable materials such as pyrites are much less acted upon by bromine than by chlorine. In fact it is possible to treat with bromine water pyrites containing gold and extract most of the gold as bromide without attacking much pyrites, which it is not possible to do with chlorine water.

Bromine dissolves gold more easily than chlorine. The experiments made by T. K. Rose, at the Royal Mint in England, recorded in his "Metallurgy of Gold," page 242, show that a saturated solution of chlorine in water, that is about 0.76 per cent. of chlorine, dissolved 57.6 parts of gold, while a two-tenths per cent. solution of bromine in water, less than one-third the strength of the chlorine, dissolved under exactly similar circumstances, 58.1 parts of gold.

These facts will render it very evident that if some means can be devised for recovering the bromine which has been used in the treatment of the ore much better results can be obtained than can be obtained by chlorination. Several plans have been devised for accomplishing this result, but only one has as yet been put into practical working in a mill. It consists in adding to the liquor which has acted upon the ore, and which stills contains a large excess of bromine as well as some bromides, sufficient chlorine or oxidizing agent and acid to liberate the bromine from the bromides and then to distil off the bromine by steam. The amount of liquid which it is necessary to distil off in order to free an aqueous solution of bromine from its bromine is surprisingly small. Using a solution of about fifteen pounds in 100 gallons the bromine is practically gone when about five per cent. of the liquid has distilled over. The liquid thus freed from bromine is in an ideal condition for the precipitation of gold, and this may be accomplished by any convenient method. It will then be seen that the process is in the main identical with chlorination as far as apparatus is concerned, except that to the liquid an addition of chemicals is made and

it is then heated up by steam and a small portion distilled off before precipitation.

The necessary steps may be stated as follows:

1. Crushing the ore preferably in a Blake crusher.
2. Drying.
3. Reducing to twenty to thirty mesh preferably by rolls.
4. Roasting, unless it is already almost completely oxidized.
5. Treating with bromine solution, preferably by agitation in a barrel, under some circumstances also by percolation in vats.
6. Drawing off the liquor and washing the ore with weak wash water from a previous operation, and after that either with water, or else with liquor from which the gold has been precipitated in a previous operation.
7. Adding to the strong liquor from leaching the ore sufficient chlorine, bleaching powder and acid, potassium permanganate and acid, or some other oxidizing agent, in sufficient quantity to liberate the bromine present as bromides.
8. Distilling off the bromine by steam.
9. Precipitating the gold.

With regard to the reduction of the ore to a proper fineness nothing need be said. It should be done exactly as if the ore were to be treated by chlorination.

The roasting, however, need not with ores which lose gold on roasting be carried so far as if the ore were to be chlorinated. The reasons why this is true are evident from a consideration of what has been said with regard to the differences in properties between chlorine and bromine; the less powerful oxidizing action of the bromine, the greater solvent power on the gold, and above all the possibility of making a strong solution of bromine, while in chlorination the solution is weak, render it possible to stop the roasting at a very much less perfect degree. The advantages of this will be apparent when the losses in gold, which occur during the last stages of roasting, are taken into account,[1] losses which result both from the volatility of the gold itself, and also from the fine particles being carried away by the current of air in the furnace. In roasting tellurides especially the losses in gold are enormous if the roasting is carried

[1] Rose, Metallurgy of Gold, p. 222.

too far. Küstel records the loss of twenty per cent. of the gold present during the oxidizing roasting of certain tellurides of gold and silver, and states that it is not a mechanical loss, but is due to volatilization. Rose records many other results which place beyond doubt the great advantage of restricting the roasting as much as possible. This loss of gold toward the end of the roasting causes one of the greatest difficulties in chlorination. Since one per cent. of sulphur requires 200 pounds of chlorine per ton of ore, the loss must be borne because it is necessary to carry on the roasting to a high degree, otherwise no gold at all, or only a part, will be obtained.

The mechanical treatment of the ore during the action of the bromine upon it is not different in any material way from the treatment with chlorine; the ore is charged into the barrel in the same way. The bromine solution is added at the bottom, through the pipe which serves to draw it off again after the treatment. If the percolation process in vats is used the bromine solution is introduced into a covered vat, using the same precautions to avoid packing of the ore, etc., that are now used in the vat process for chlorination, and in the cyanide process.

After the ore has been acted upon by the bromine solution for a sufficient length of time the liquor is drawn off at the bottom and weak wash water from a previous operation introduced at the top of the ore, the first liquor, which is strong, being sent to a strong liquor tank, and the subsequent weaker liquor being reserved in a weaker liquor tank for subsequent use in leaching ore. From the strong liquor tank the solution runs into a still. One form of apparatus which has been used successfully, but which is now being superseded by an improved form consists of a covered stone tank heated by live steam, and provided with an outlet for the vapors, which leads to a stoneware condenser. Into the condenser, weak liquor from the weak liquor tank is allowed to enter with the vapors and in this way a bromine solution of the proper strength to run into the barrel with more ore is obtained. To the liquid in the still, before steam is turned on, bleaching powder and oil of vitrol, or

potassium permanganate and oil of vitrol, is introduced in sufficient quantity to free the bromine present as bromides. The chemicals used for this purpose in the mill have been bleaching powder and oil of vitriol. It may be asked why, if bleaching powder and acid are to be used to liberate the bromine from bromide, it would not be just as well to treat the ore with them in the first instance; to this it may be answered that in the process only as much chlorine is used as will liberate the amount of bromine which has actually combined with the ore, whereas in chlorination an excess is used which amounts to several times this amount. After the bromine is out of the liquid in the still it is run hot into the precipitating tanks, where it may be precipitated in any desired way. The only difference between the precipitation here and in chlorination is that here there is no troublesome excess of chlorine to be disposed of by sulphur dioxide or to use up large quantities of precipitants. The precipitant actually used in the mill has been powdered sulphide of iron, which in the hot liquor precipitates the gold quickly and completely. The gold is caught in a filter press and refined as usual.

Where ores are to be treated, in which the gold is present partly in too large pieces to dissolve rapidly in the bromine solution, the washed ore must be allowed to run over amalgamated plates, and as the gold is in perfect condition to amalgamate, it is easily caught.

The details of the process have been worked out by the Nellie Bly Gold Mining & Reduction Co., in Magnolia, Colorado, using an ore which has never before been successfully treated. It is a siliceous ore containing from $8.00 to $20.00 in gold per ton as tellurium compounds and nothing else of value. It cannot be amalgamated, concentrated, treated by the cyanide process, nor shipped to the smelters in Denver at a profit, and consequently presents a very difficult problem which has, however, been solved with entire success.

The process is also about to be introduced in other localities, and it seems entirely probable that it may in the near future displace chlorination to a great extent, at least.

SCHOOL OF MINES,
COLUMBIA UNIVERSITY, N. Y.

A SIMPLE METHOD FOR DETERMINING THE NEUTRALITY OF THE AMMONIUM CITRATE SOLUTION USED IN THE ANALYSIS OF FERTILIZERS.

By N. W. Lord.

Received April 6, 1896.

IT is well known that the preparation of a strictly neutral solution of ammonium citrate requires considerable judgment, owing to the uncertainty of the color change when using ordinary indicators in the presence of salts of citric acid.

Even when using corallin, as directed in the official methods of the Association of Official Agricultural Chemists, some uncertainty remains. "Huston's Method" with alcoholic solutions of calcium chloride, while very exact, is a little troublesome.

The following method has been in use in my laboratory for over a year and has proved rapid and exact. I have used it only with litmus as the indicator as the tint so obtained is very easily matched, probably corallin or cochineal would do as well.

The method consists in establishing an accurately neutral color for comparison, by superimposing two tubes, one containing acid litmus, and the other alkaline litmus, and looking through both at once. Then comparing this with the diluted citrate solution, colored to the same depth with the same amount of litmus tincture. The details are as follows:

Add pure litmus solution to about 200 cc. of neutral distilled water until it is colored distinctly, but not deeply. Take half of this and dilute further with its own volume of water. Now take three clear fifty cc. "Nessler tubes," fill two of them with the diluted liquid, and the third to the same depth with the stronger solution. To one of the two first add a drop of dilute sulphuric acid, to the other a drop of ammonia. Set these tubes one in front of the other, so that the light passes through both, thus giving a strictly neutral purple color; a little care will enable one to see them almost like one tube against a sheet of white paper in a ground glass. It makes no difference which tube is in front. Now to the liquid in the third tube containing the stronger solution (which is obviously equal in color depth to the double thickness of the first two tubes), add five cc. of the citrate solution to be tested, and compare the color

produced with the color shown by the doubled tubes. The slightest acidity or alkalinity of the citrate is at once shown by difference of tint; the test is very sensitive. The amount of acid or alkali needed to bring it right, can then be easily obtained by adding one-half normal sulphuric acid or ammonia; then by calculating to the five cc. taken, the necessary addition to the "stock" solution can be found and when made the solution re-tested with remainder of the colored water. The operation is very rapidly performed and the results surprisingly exact. Solutions so neutralized, when tested by Huston's method, have always been found exactly correct. The litmus solution should be prepared from the alcohol extracted litmus, as directed by Sutton.

THE COPPER ASSAY BY THE IODIDE METHOD.

BY ALBERT H. LOW.

Received March 23, 1896.

THE last edition of Dr. Peters' Modern Copper Smelting contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstandiug that the latter, when every precaution is taken, is perhaps theoretically more accurate.

COPPER ASSAY BY THE IODIDE METHOD.

Prepare a solution of sodium hyposulphite containing about nineteen grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Add five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and thoroughly boil off the red fumes,—a very essential point. Now remove from the lamp and add six to seven grams of crystallized zinc acetate, roughly weighed, and about fifteen cc. of water. Instead of adding the of zinc acetate in this way, a cold saturated solution may be kept on hand and about twenty

cc. taken, the additional fifteen cc. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about fifty cc. Now add about three grams of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated and iodine liberated according to the following reaction: $2(Cu.2C_2H_3O_2)+4KI=Cu_2I_2+4(K.C_2H_3O_2)+2I$. The free iodine colors the mixture brown. Titrate at once with the hyposulphite solution, until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One cc. of the hyposulphite solution will be found to correspond to about 0.005 gram of copper. In the assaying of ores, etc., when half a gram is taken, one cc. of the standard hyposulphite would then equal about one per cent. copper. The reaction between the hyposulphite and the iodine is: $2(Na_2S_2O_3)+2I=2NaI+Na_2S_4O_6$. Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a gram of starch with a little water and diluting with hot water to about 250 cc. It should be used cold and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

TREATMENT OF ORES.

Treat half a gram of the ore in a flask of 250 cc. capacity with five or six cc. of strong nitric acid and boil gently nearly to dryness. Then add five cc. of strong hydrochloric acid and again boil. As soon as the incrusted matter has dissolved add five cc. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool and then add twenty cc. of cold water and heat the mixture to boiling to thoroughly dissolve any anhydrous sulphates of iron, etc. Now

filter to remove more especially any lead sulphate and receive the filtrate in a beaker about two and one-half inches in diameter. Wash the flask and filter with hot water and endeavor to keep the volume of the filtrate down to about fifty or sixty cc. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows: Stout sheet aluminum, say about one-sixteenth of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add five cc. of strong sulphuric acid, cover the beaker and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a wash bottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible and temporarily set it aside with the aluminum which may still retain a little copper. Allow the copper in the flask to settle and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally wash the filter once or twice and endeavor to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main

portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling and see that all the copper is dissolved. Then add about half a gram of potassium chlorate and again boil for a moment. This is to oxidize any arsenic present to arsenic acid and is a very important point. Remove the flask from the lamp and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate and proceed from this point precisely as described with the original nitrate of copper solution in the standardization of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a gram of pure copper requires 2.62 grams of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than three grams of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuch is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidized as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance, but a quick return of the color, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions

given and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, etc., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of five cc. of dilute nitric acid for dissolving the copper previous to titration and prescribes six to seven grams, or about twenty cc. of a saturated solution of zinc acetate as a safe excess of neutralizing agent. It is obvious that if most of the nitric acid be boiled away the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.

DENVER, COLORADO.

ON TWO SOURCES OF ERROR IN SUGAR HOUSE ANALYSES.

BY EDMUND C. SHOREY.

Received March 10, 1896.

INCIDENTAL to the study of the action of water of different temperatures on bagasse, I have had occasion to make some determinations which throw some light on a source of error in fiber determinations.

Finely cut cane was washed with cold water until the polariscope reading in a twenty cm. tube was 0; the excess of water squeezed out in a press, and three portions of fifty grams each taken. In one the moisture was determined by drying to constant weight in an air bath at 105° C.; the two others were treated with boiling water; one for five minutes and the other for two hours. The quantity of water used was in each case just sufficient to cover the cane chips, and at the expiration of the time the water and the chips were poured on a filter and washed four times with cold water, using each time the same quantity of wash water as was used in the original treatment. The filtrate so obtained was evaporated to dryness over a water-bath, dried at 105° C., and calculated to percentage of dry sub-

stance left after the exhaustion of sucrose with cold water. The filtrates obtained were decidedly milky, and this no amount of filtering would remove. A portion of filtrate on standing undisturbed for six days had *not* become less milky, and had thrown down *no* deposit.

The cane was prepared by cutting to fineness of saw dust in a meat chopper, and determinations have in all cases been made in duplicate.

The mean of six fairly mean concordant determinations is as follows :

(1) Treatment for five minutes with boiling water extracted seven and two-tenths per cent. of dry substance.

(2). Treatment for two hours with boiling water extracted twelve per cent. of dry substance.

To show the amount of error likely to result from using varying quantities of water and varying the time of boiling ; suppose that the fiber and dry substance from the treatment with cold water was ten per cent. of cane, we would have :

	Per cent.
Fiber extraction with cold water	10.0
" " " hot water five hours	9.3
" " " " " two hours	8.8

Dr. Beeson, of Audubon Park Sugar School, has pointed out in this Journal the errors in fiber determinations likely to result from the varying amounts of fiber in different parts of the same stalk of cane. This can be overcome, I think, by taking a sufficiently large sample and reducing it to a very fine state of division; but if fiber determinations by different chemists are to be comparable, some uniform method must be agreed upon. This method should provide for the fineness of division of cane or bagasse, the quantity of sample to be taken, the quantity of water to be used, the number of times washing, and the length of time of boiling.

In calculating the extraction by formulas similar to those given by M. Trubek in this Journal (Dec., 1895), I prefer to dry the residue from alcoholic extraction and call this fiber. The object being simply to compare the fiber in the cane with that in the

bagasse, and this method I find gives more uniform results with a minimum of labor.

A second source of error in sugar house analyses to which I wish to draw attention is in the determination of albuminoid nitrogen as commonly carried out.

In the official method for albuminoid nitrogen in finding stuffs the directions are to heat to boiling, add cupric hydrate, filter when cold and wash with cold water. In the determinations of albuminoid nitrogen in cane juice made by W. Maxwell, and published by him in a Bulletin of Louisiana Experiment Station, this method was modified, but for what reason I am unable to say. According to this modified method the juice was heated to boiling, cupric hydroxide added, boiled ten minutes, filtered hot and washed with hot water. Both these methods introduce a serious error, owing to the fact that when cane juice in its natural acid condition is heated a change is brought about in the aluminoid nitrogen contained therein, and in consequence the amount of aluminoids as determined by either of these methods is not really that which is in the juice in the plant, but that which is left from the action of heat and the acid in the juice.

During the past two years I have made a large number of determinations, as follows: I. Total nitrogen in juice; II. Albuminoid nitrogen in cold juice; III. Albuminoid nitrogen in juice which had been heated to 71°–72° C.; IV. Albuminoid nitrogen in juice which had been boiled one minute. For total nitrogen the Gunning method was used, and for albuminods cupric hydroxide was added to cold juice, filtered cold and washed with cold water, the precipitate and filter paper treated by Gunning method. In each case twenty cc. of juice have been used, and the results calculated to percentage of total solids as given by Brix spindle; the difference between total nitrogen and albuminoids has been called amides and calculated to asparagins.

As the results have been the same in all cases, I give below two analyses which I have already communicated to the Planter's Monthly, (Honolulu).

1. Brix, 17.3; Purity, 91.

Acidity, 100 cc. juice = ten cc. $\frac{N}{10}$ alkali.

Total nitrogen 1.115 per cent. of total solids.

	Per cent. of nitrogen compounds.	
	Albuminoids.	Amines.
Cold juice	95.5	4.5
Juice heated 71°–72° C	87.5	12.5
Juice boiled one minute	86.7	13.3

2. Brix, 18.2; Purity, 90.9.

Acidity, 100 cc. juice = 11.3 cc. $\frac{N}{10}$ alkali.

Total nitrogen 1.032 per cent. of total solids.

	Per cent. of nitrogen compounds.	
	Albuminoids.	Amines.
Cold juice	93.5	6.5
Juice heated 71°–72° C	81.4	18.6
Juice boiled one minute	77.4	22.6

Although I have in these analyses designated the body or bodies formed from the albuminoids by heat amines, I am of the opinion for several reasons that they are peptones or soluble albuminoids. I am at present investigating the matter. Whatever they are, the fact remains that the albuminoid nitrogen determinations on cane juice as carried out by any method which calls for the heating of the raw acid juice are not reliable.

LABORATORY KOHALA SUGAR CO.,
KOHALA, HAWAII.

REVIEW.

BERTHELOT'S CONTRIBUTIONS TO THE HISTORY OF CHEMISTRY.[1]

Marcellin Berthelot, Professor of Chemistry in the Collège de France, Perpetual Secretary of the Academy of Sciences, Senator, Minister of Public Instruction, and recently appointed Minister of Foreign Affairs, known to the scientific world by his masterly researches in synthetical chemistry, has added to these honors that of editing the most important and far-reaching documents pertaining to the history of chemistry ever brought to light.

The six handsome quarto volumes published by him between the years 1887 and 1893, contain the most ancient Greek, Arabic, Syriac, and Latin treatises on alchemy and technical chemistry preserved in the great libraries of the Old World. Besides reproducing the original text of these precious manuscripts, these volumes contain complete translations of many treatises, analyses of the contents of others, and critical studies of their mutual relations, their sources and authorship, as well as erudite essays on the chemical knowledge exhibited in them. The six volumes form two distinct works: three of the volumes bear the title: "Collection des anciens Alchimistes Grecs," and three of them, "La chimie au moyen âge," each volume having, moreover, specific sub-titles more exactly indicating its contents.

Not having seen any adequate review of these works in English, I propose in this article to examine their scope, contents, and manner of treatment, as well as to show some of the more important changes resulting from Berthelot's historical studies. The existence of ancient Greek and Arabian manuscripts had long been known; Reuvens, and later Leemans, of Holland, had published summaries of certain papyri preserved in Leyden, more than forty years before, but in such a fragmentary manner as merely to excite curiosity. Ferdinand Hoefer, the French historian of chemistry, and Herman Kopp, the erudite German, had made partial use of some of the manuscripts, but it remained for Berthelot to collect and compare the diverse copies, to reproduce and translate them for the benefit of students. This he could scarcely have accomplished without the aid of the French Government, both series being "published under the auspices of the Minister of Public Instruction." Government cooperation was brought about through a report made by Berthelot to

[1] Read before the Washington Section of the American Chemical Society, March 12, 1896.

the "comité des travaux historiques et scientifiques," and adopted by them in 1884. This report directed attention to the existence of Greek alchemical manuscripts and to the utility of their publication, owing to the great light they throw on the history of natural science, the technology of metals and ceramics, and the history of philosophy in the first centuries of the Christian era.

The difficulties of deciphering, transcribing, and editing Greek, Arabic, Syriac and Latin manuscripts were prodigious, and Berthelot was fortunate in securing scholars of eminence to assist in the task. In dealing with the Greek papyri, he was aided by Ch. Em. Ruelle, of the Bibliothèque Sainte Geneviève, Paris, and by André Berthelot, son of the editor; the Arabic scholar, Professor Houdas, and the Syriac linguist, Rubens Duval, also contributed their learning, each in his own sphere.

The "Collection des Alchimistes Grecs," opens with an "Introduction" by Berthelot, which occupies 268 pages; this forms an important contribution to the history of chemistry, based upon a critical study of the ancient treatises; he agrees with other historians in tracing the birth of alchemical ideas to Egyptians, whence they reached Europe through Greeks.

Certain Greco-Egyptian papyri, preserved in Leyden, are of the greatest interest; several of them treat of magical formulas, incantations, love philtres, dreams, and similar gnostic notions; one of them, known as "Papyrus X," is a treasury of information on metallurgical operations, at so early a period as the third century of the Christian era. It was found in a tomb at Thebes, secured by the Swedish Consul at Alexandria, Anastasi, and presented by him to the Netherlands in 1828. Berthelot conjectures it is one of the ancient Egyptian books on the preparation of gold and silver, which escaped the destruction ordered by Diocletian in 290; an order issued lest the people using them should grow rich by their art and revolt against the Romans.

This precious document contains one hundred and one chemical and alchemical recipes, followed by ten paragraphs taken from Dioscorides. The recipes are for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art, also processes for soldering metals and superficially coloring them, besides formulas for making gold and silver inks. The text is full of grammatical errors and ignorant spellings, which show the writing to have been the work of an uneducated artisan; the recipes are not arranged in order, several appear in duplicate; they exhibit no indication of chicanery, although some of the methods are unprofitable. The

whole papyrus, in short, is evidently the memorandum-book of a goldsmith (or silversmith), engaged in attempts to imitate gold and silver for fraudulent purposes. Only one author is cited, "Phimenas," who is probably Pammenes, author of recipes occuring also in other manuscripts. The preparation of *asem*, an amalgam of copper and tin, plays a prominent part among the recipes for imitating gold. But time forbids a full analysis of this remarkable manuscript; as a result of Berthelot's careful study of this and analogous treatises, he comes to the conclusion that the doctrines of alchemy concerning the transmutation of metals did not originate in the philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of goldsmiths occupied in making fraudulent substitutes for the precious metals. The "Introduction" contains a chapter on the relations between the metals and the planets, of Chaldean origin, and constant occurrence in the early writings, which is illustrated by facsimiles of several manuscript pages. Another chapter is devoted to the figures of apparatus occurring in the treatises of the eleventh to fourteenth centuries; these include water-baths, digestors, aludels, alembics and a great variety of apparatus for distillation.

The sixth chapter of the introduction is divided into twelve sections; these deal with several Greek manuscripts, notably those preserved in the libraries of St. Mark, Venice, the Escurial, the Vatican, Rome, Gotha, and in Munich, appertaining to the eleventh to fourteenth centuries; of these we note only a few features. At the beginning of the MS. of St. Mark is one of the earliest of chemical bibliographies; it gives the title of fifty-two treatises, verily not in modern style, yet quite suggestive; among them are the following: "Emperor Heraclius, eleven chapters on the manufacture of gold." "Justinian, five chapters on the secret art." "Heliodorus, on the divine art." "Theophrastus, verses on this art." "Moses, on the diplosis (doubling) of gold." "Lexicon of the gold maker, in alphabetical order."

This association of names of Emperors of Rome, Greek classical writers and the Hebrew law giver with chemical and alchemical treatises is characteristic of the period at which they were compiled and by no means denotes actual authorship; the names of prominent men were given to the treatises in order to add to the dignity and authority of the writings. This custom prevailed as late as the sixteenth century, and in certain cases to be noted hereafter, gave rise to undeserved honors. An entire group of writings have been ascribed to Democritus, giving rise in Egypt to what may be styled the school of Democritus. A certain Zosimus of Panoplis is credited with a veritable ency-

clopedia of the sacred art, a work which occupies ninety pages of Berthelot's volume.

The Collection des Alchimistes Grecs comprises no less than 160 different treatises on the science of Hermes. Many of these are fragmentary in the extreme, extending to only six lines, and even less. All are composed in an archaic, enigmatical style, combining in one undecipherable medley, chemical terms of obscure meaning, magical formulas, astrological notions, citations from mythical authors, and mystical allusions to a philosophy long since buried too deep for present resurrection. It is not surprising that commentators early felt the need of lexicons of the sacred art, and such are preserved in these volumes; unfortunately, however, the definitions are no clearer than the words defined; one word was often used for a score of different objects and processes, and a single article was known by a dozen different names. To convey to readers any idea of these extraordinary literary productions by citations, is hardly practicable in the space available, for passages lose much when removed from their original settings. The actual chemical knowledge exhibited in these ancient manuscripts is varied, and yet indefinite, owing to the numerous obscure expressions; the authors were acquainted with a large number of ores, minerals, earthy substances, and saline bodies, as well as vegetable and animal products, but their ignorance of the mineral acids and their important derivatives, limited them to products obtained by aqueous solution, distillation and the action of heat. Of scientifically classified knowledge there is no trace; the alleged opinions of mythical writers are given as authoritative, and information is imparted in the tedious form of dialogues between philosophers, who remind one of the Scotchman's definition of metaphysicians: "Poor bodies discussing things of which they know nothing, in a language neither of them can understand." Many of the writings contain reverent acknowledgements of the Deity and other evidences of piety. There is a good deal of duplication, arising from the introduction into an essay of passages from another, generally without acknowledgement.

Berthelot remarks incidentally that the term *Philosophers' Stone* does not occur in writings earlier than the seventh century, although the central idea is much more ancient.

Each of the three quarto volumes which constitute Berthelot's "La chimie au moyen âge" bears an independent title; that of the first volume reads: "Essay on the transmission of the knowledge of Antiquity to the Middle Ages; transmission of technology; translations of Arabico-Latin treatises, with a new

version of the *Liber Ignium* of Marcus Graecus, and an original edition of the *Liber Sacerdotum*."

This volume covers the period from the fall of the Roman Empire to the thirteenth century, thus filling the gap between the ancient Greek alchemists and the Latin writers of the later epoch, a period which had been previously unworked or misunderstood. Berthelot finds that the transmission from the earlier to the later era was accomplished by two agencies; first through the Arabians, who succeeded to the literary and scientific wealth of the Greeks. The Arabic treatises, preserved in the Mohammedan libraries of Spain, were translated into Latin and thus became for Western nations the sources of their knowledge in medicine, alchemy, mathematics and philosophy. Some of these translations were collected and printed in the seventeenth century in the works entitled *Theatrum chemicum*, (5 vols., 1613–22), and *Bibliotheca chemica*, of Mangetus, (2 vols., folio, 1702), and Berthelot discovered in these Arabico-Latin treatises entire passages from the ancient Greek Alchemists.

The connection between the Greeks and Arabians was not however immediate, but through the Syrians, who were among the first to translate the philosophy and science of the Greeks into an oriental tongue. These Syraic versions form the subject of the second volume.

A second link between the Greeks and the Latin alchemy was more directly forged, though difficult of recognition; the processes used in industrial arts and metallurgical operations by the Greeks had been adopted by the Latins as early as the time of the Roman Empire, and this chemical technology was preserved through centuries of intellectual degradation to the beginning of the Middle Ages.

The most ancient Latin treatises on chemical technology are the *Compositiones ad tingenda*, dating from the close of the eighth century, and the *Mappæ clavicula*, written before the tenth century. These are collections of recipes for industrial processes analogous to those in the Leyden papyrus, and forming links in a chain that extends from that ancient work through the treatises of the Middle Ages to the modern "Workshop Recipes" and "Manuels Rorets." The full title of the *Compositiones ad tingenda* is as follows: [Translation.] "Recipes for coloring mosaics, skins and other objects, for gilding iron, for using minerals, for writing in letters of gold, for soldering metals, and other technical documents." The following are some of the subjects treated: The coloring of artificial stones, used in the manufacture of mosaics; the manufacture of stained glass; the dying of skins in purple, green, yellow and reds; the dyeing of

wood, bone and horn; a list of ores, metals, earths and metallic oxides used in jewelry and in painting; a number of recipes for gilding on glass, wood, skins, garments, and the metals. All these topics are treated in barbarous Latin, bordering on a species of jargon; some were originally written in Greek and copied by ignorant scribes in Latin letters, which shows the influence of Constantinople. In one of the sections on ores, the word "vitriol" occurs for the first time, being the eighth century, and in the correct significance of an impure ferrous sulphate. A very rational grouping of substances occurs in this work, the minerals and earths are by themselves, then follow gums, rosins and other products of plants, and thirdly substances derived from the ocean, such as salt, coral and mollusks yielding purple dye. A certain recipe for writing in letters of gold is practically identical with one in the Papyrus of Leyden.

A formula for making bronze shows the origin of this name, *De compositio brandisii*, Brindes being a synonym of Brundusium, (Brindisi), a town noted in Pliny's day for its metallic mirrors.

A large part of *Compositiones ad tingenda* is reproduced in the work entitled *Mappæ clavicula*, of which the earliest known manuscript dates from the tenth century. This latter treatise contains recipes for making gold, for multiplying gold and imitating the precious metal, closely resembling those of the ancient Greek papyri. In this connection cautions are given to conceal the secrets, and an incantation is prescribed to be used during the operation. Exceeding interest attaches to the fact that the use of the hydrostatic balance in analysis of an alloy is clearly described, for this proves that the knowledge of this instrument did not pass through Arabian channels, and possibly came down direct from Archimedes.

The *Liber ignium ad comburendos hostes*, by Marcus Graecus, is one of the most ancient Latin treatises on Greek fire, dating from the twelfth or thirteenth century, and is probably a translation from an earlier Greek work transmitted through Arabian channels. It deals with instructions for making Greek fire, so called, phosphorescent materials, fire-proofing substances, and the preparation of fuses and petards, composed in part of saltpeter. Greek fire itself, however, dates from the second century, B. C., and phosphorescent stones are named in the much earlier Greek alchemical manuscripts.

Berthelot devotes an interesting chapter to the discovery of alcohol. This product of distillation first appears under the name *aqua ardens*, and the term alcohol in its present signification does not occur before the middle of the fourteenth century; the

term *spiritus vini* is also comparatively modern, and *aqua vitae* seems to have been applied to alcohol for the first time by Arnald de Villanova, who died in 1314. The fact that wine yielded an inflammable substance, was, however, already noted by Aristotle, but this body was not isolated. Rhases has been given credit for acquaintance with alcohol, but this is erroneous.

The preparation of alcohol by distilling wine is, however, mentioned in a copy of the *Mappæ clavicula*, written in the twelfth century, and in the *Liber ignium* of Marcus Graecus.

In attempting to trace to their origin, Latin treatises which claim to be translated from Arabic, Berthelot made the important discovery that they are fraudulent, the Arabic manuscripts having no existence. Thus the chemical works attributed to the Arabian physician Jâbir ibn Hayyan (Abu Musâ), commonly called Geber, are shown to be fictitious, and the great reverence paid to him as a pioneer in chemistry has been misplaced. The whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

Yet the historical personage Geber, who lived in the ninth century, left many treatises in Arabic, now preserved in Paris and Leyden, and the translation of these occupy 100 pages of the third volume; they are very different from the works so widely known as Geber's, which are found in Latin, French, German, and English.

In like manner the current alchemical treatises ascribed to Raymond Lully are shown to be fictitious, yet his works on philosophy in the Provençal language are extant.

The Pseudo-Arabic works in their Latin form contain, however, traces of the ancient Greek alchemical writings, and to endow them with authority the writers referred the text to mythical personages; and as these were cited by later authors who did not doubt their genuineness, the pseudo-treatises acquired undeserved renown. Students of alchemy who have been revelling in the works of Morien, Kalid, Zadith, Mary, and the collection of citations entitled *Turba philosophorum*, are loth to have their antique idols shattered, but this is the fate of every branch of human knowledge when subjected to the modern methods of searching analysis.

The second volume of "La chimie au moyen âge" has the subtitle: Syriac Alchemy, comprising an introduction, and several treatises of Syriac and Arabic alchemy from the manuscripts in the British Museum and Cambridge; text and translation."

The existence of Syriac alchemical manuscripts in the British

Museum was pointed out to Berthelot by Prof. Richard Gottheil, of Columbia University, New York City. The most important of these, entitled "The Doctrine of Democritus," was translated from Greek between the seventh and ninth centuries. It begins with a charge of self-purification, followed by a key to the symbols used in the manuscript; these signs resemble in part those occurring in the writings of the earlier Greek alchemists. The first section of the "Doctrine" is called "The Preparation of Gold," the second is called "On the Philosophers' Stone," and the succeeding parts contain a collection of recipes, processes with metals, as well as with sulfur, antimony, arsenic, and ores, analogous to the Leyden papyrus and the *Mappæ clavicula*. Rude drawings of apparatus accompany the text. The writer shows acquaintance with a very large number of chemical substances.

The Library of the University of Cambridge possesses a Syriac manuscript, which is a translation of portions of the Greek writings of Zosimus, Democritus, and others. It is similar in character to the preceding.

Volume III of "La chimie au moyen âge" has the sub-title: "Arabian Alchemy, comprising an historical introduction, the treatises of Crates, el-Habîb, Ostanes and Djâber from manuscripts in Paris and Leyden; text and translation."

The Arabic treatises here named are the genuine writings, not the fictitious ones known only in Latin. The first Mohammedan writer on alchemy was Khâled ben Yezid ibn Moaouïa, Prince Omeyyade, who died in 708; he is a historic personage and the reputed teacher of Djâber. Only the titles of his works have come down to us. Djâber, the Geber of the Latins, was, however, the great master of the art and enjoyed the highest reputation throughout the Middle Ages; he is credited with 500 treatises, an Oriental exaggeration. Six of these are here collected and translated. They exhibit evidence of Moslem faith on the part of the author; he shows familiarity with the hydrostatic balance, with many species of minerals (of which an ingenious classification is given), and he discourses on the changes in volume produced by heat and by cold; at the same time he admits using allegorical and obscure language in all his works. There is no reference to the mineral acids, to nitrate of silver and other chemicals that Geber is supposed to have known. Perhaps the most clever passage in his works is the following from the "Book of Mercy:"—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I

then perceived that they were divided into two categories, the dupers and the duped. I had pity for both of them."

Berthelot's superb volumes comprise more than 2600 pages, and much of the contents defies review. Besides these original documents he has published two works dealing in more popular style with the periods of alchemy and Middle Age chemistry. These are entitled: "Les Origines de l'Alchimie," (1885), and "Introduction à l'Étude de la Chimie des Anciens et du Moyen Age" (1889); the latter is largely reprinted in the quarto volumes; all are charmingly written, well illustrated, and well indexed.

Berthelot had extraordinary qualifications for the task and enjoyed unrivalled opportunities, and the result is a magnificent contribution to the history of chemistry, of utmost interest to the chemical student as well as to the philosopher.

H. CARRINGTON BOLTON.

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Bulletin No. 36. Imported Elm Leaf Beetle, Maple Pseudo-coccus, Abbot Sphinx, San Josè Scale. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass. February, 1896. 20 pp.

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Bulletin No. 62. Strawberries. Kentucky Agricultural Experiment Station, Lexington, Ky. March, 1896. 16 pp.

Bulletin No. 21. Field Experiments with Wheat. Missouri Agricultural College Experiment Station, Columbia, Mo. April, 1893. 16 pp.

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Bulletin No. 37. Sundry Brief Articles, compiled from "Press Notes" published during the years 1894 and 1895. Texas Agricultural Experiment Station, College Station, Brazos County, Texas. 83 pp.

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Bulletin No. 40. Cow Pea. Agricultural Experiment Station, Baton Rouge, La. 30 pp.